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(54) Title: DOSING OF PEROXIDE TO A SUSPENSION PROCESS WHEREIN STYRENE IS POLYMERIZED

(57) Abstract: The invention relates to a suspension polymerization process for the preparation of styrene-containing (co)polymers, wherein the process comprises the steps of continuously or semi-continuously dosing an initiator to the reaction mixture, said initiator having a specified half-life at the temperature of the reaction mixture to which it is dosed. The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.

WO 2004/089999 A2

DOSING OF PEROXIDE TO A SUSPENSION PROCESS WHEREIN STYRENE IS POLYMERIZED

The invention relates to an essentially vinyl chloride-free batch process for polymerizing, in a suspension, styrene monomer, or a mixture of monomers comprising styrene, for the preparation of styrene-containing (co)polymers, wherein the process comprises the step of continuously or semi-continuously dosing an initiator to the polymerization mixture at the polymerization temperature. The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.

Processes for polymerizing styrene monomers are known in the art, for instance from US 4,363,881 and US 6,153,658. Here a conventional process is described wherein peroxide is added at two points in a batch suspension process, but wherein the peroxide is not dosed. US 5,189,069 suggests to dose an initiator dissolved in monomer to obtain styrene beads with a controlled particle size. Conventional initiators are used that have a half-life of more than one hour at the dosing temperature. Comparable processes are disclosed in EP-A-0 234 705 and in EP-A-0 488 025, wherein use is made of a different method, i.e. seeding the reaction mixture with substantial amounts of polymer seed particles before the continuous addition of an initiator solution in monomer(s) is started. Also in EP-A-0 234 705 the initiators that are dosed have a half-life of more than one hour at the dosing temperature. Another process to prepare a suspension of polystyrene is described in US 5,905,096. Here a prepolymer comprising peroxide and blowing agent is formed, which is subsequently suspended and reacted to completion. All these methods are aimed at particle size control, but they suffer from the disadvantage that pre-determining the molecular weight of the polymer and controlling the rate of polymerization is difficult, if not impossible. In addition, these methods require a long polymerization time and typically comprise more than one reaction step, and often the initiator is to be added as a solution in monomer, which can show undesired (pre)polymerization before it is added to the reactor and, therefore, may not be safe.

It is an objective of the invention to provide a method of polymerizing styrene monomer for the preparation of a styrene-based (co)polymer, also referred to in the this description as "polystyrene", with good control of the molecular weight and the molecular weight distribution, so that a polymer is obtained which is comparable to the polymer of the conventional process, but requiring a shorter polymerization time. In the process at least one initiator is used that is wholly or partially dosed while fulfilling the requirements of the present invention. More specifically, the at least one initiator being dosed is to be chosen such that, given the specific polymerization temperature profile, the half-life requirements are met. This initiator is called "the initiator" in the remainder of the application. The invention also encompasses a process wherein a combination of initiators is dosed, as long as the combination of initiators comprises "the initiator". It is noted that the term "the initiator" from this point on encompasses such combination of initiators. Also it is noted that "the initiator" can be used in combination with an additional initiator. In that case the latter may be dosed separately or just added, without being dosed.

In the process of the invention the molecular weight and the molecular weight distribution of the polystyrene in a polymerization process of styrene monomer can be controlled, while the overall space-time-yield of the polymerization equipment is increased.

It is noted that this process does not require the use of a pre-polymerization process or the addition of seed particles. However, if so desired, polymer particles, especially particles of an undesired particle size resulting from earlier polymerization batches, may be recycled. If used, the particles are preferably dissolved in the monomer for more than 50% during the heating of the reaction mixture to the polymerization temperature.

It is further noted that WO 00/17245 discloses a process wherein vinyl chloride can be copolymerized with styrene in a suspension process wherein peroxide is dosed. The present process differs from the process of WO 00/17245 in that it is

essentially vinyl chloride-free, meaning that the amount of vinyl chloride is less than 1% by weight, preferably less than 0.1% by weight, based on the weight of all monomer. Preferably, the process of the present process is completely free of vinyl chloride, to avoid pressure build-up in the process and to avoid environmental issues. As is known in the art, the polymerization kinetics of a vinyl chloride polymerization differ strongly from the kinetics of other ethylenically unsaturated monomers because the chain transfer to monomer reaction is prevalent in vinyl chloride-containing polymerization processes. This results in the major difference that the molecular weight of the vinyl chloride polymer is largely determined by the polymerization temperature, whereas this is not the case when a styrene polymer is formed.

During the process of dosing the initiator a polymerized product will be formed. Thus, after a certain period of time the initiator is dosed to a mixture of monomer and polymerized product. Preferably, the initiator is continuously or semi-continuously dosed over a period of at least 0.5, more preferably at least 1 hour. When larger quantities of polymer are made in a batchwise fashion, an addition time of up to 5 hours or more is possible, depending on the molecular weight required. From a commercial and a technical point of view, continuous dosing of the initiator is preferred over semi-continuous dosing.

Preferably, the dosing of the initiator to the polymerization mixture is semi-continuous or continuous over a period of time wherein at least 20%, preferably at least 40%, more preferably at least 70% of the monomers are polymerized. If a semi-continuous operation is selected, there are many (preferably 4 or more) moments at the polymerization temperature at which small portions of the initiator are dosed. If so desired, the semi-continuous and the continuous operation can be combined, such that the initiator is dosed a number of times over certain (longer or shorter) periods of time.

Most preferably, the initiator is dosed continuously or semi-continuously from the point in time at which at least 1%, preferably at least 0.5%, more preferably at

least 0.1%, most preferably none of the monomer has already been polymerized until at least 70%, preferably at least 80%, more preferably at least 90%, and most preferably essentially all of the monomer is polymerized. "Essentially all is polymerized" means that less than 1000 ppm of monomer is present in the final
5 polymerized product.

The term "continuous" also includes continuous addition at variable rates and variable time intervals. The addition of initiator at variable rates is beneficial for using the cooling capacity of the polymerization reaction in the most optimal way
10 and to prevent a so-called "run away" during the polymerization reaction. The term "semi-continuous" means an addition method wherein a number of portions of initiator are added to the polymerization mixture. If many portions are added at short intervals, the continuous addition method is being approached.

15 In one embodiment, the process according to the invention involves the polymerization of styrene-comprising monomer mixtures, further comprising co-monomers. In this embodiment it is preferred that the styrene-comprising monomer mixture comprises at least 50% by weight (wt.%) of styrene, based on the weight of all monomer. Co-monomers that can be used are of the conventional
20 type and are preferably selected from the group consisting of vinyl acetate, ethylene, propylene, acrylonitrile, butadiene, and (meth)acrylates and which includes ethylenically unsaturated polymers, such as polybutadiene and styrene butadiene rubber. Although it is less preferred, also vinylidene chloride can be copolymerized. More preferably, at least 80 wt.% of the monomers being
25 polymerized is styrene, whereas the most preferred process is a process wherein essentially all monomer is styrene.

In the process according to the invention, the half-life requirement for the initiator is such that said initiator, when present in the reaction mixture at the
30 polymerization temperature, decomposes for 50% or more (on a molar basis) in 60 minutes or less. Preferably, the half-life is less than 50 minutes, more preferably less than 40 minutes, even more preferably less than 30 minutes and

most preferably less than 15 minutes in the reaction mixture at the polymerization temperature. At the same time, the half-life preferably is more than 0.5 minutes, more preferably more than 1 minute, even more preferably more than 2.5 minutes, and most preferably more than 5 minutes in the reaction mixture at the polymerization temperature. The minimum half-life is 0.5 minutes or more, otherwise the initiator is not effective. It is believed that said inefficiency at a shorter half-life is due to the fact that the initiator should have time to migrate through the reaction mixture to the polymer/monomer phase, which is discontinuous, before it decomposes. Because redox-initiating systems typically give an almost instantaneous formation of radicals, also such initiating systems are less preferred.

It was surprising to find that a conventional styrene suspension polymerization process could be improved by using a combination of dosing techniques and selecting the proper initiator. Just using a conventional peroxide and making it decompose faster by raising the polymerization temperature resulted in a polymer with a reduced average molecular weight. Just dosing a conventional peroxide resulted in a slower, not faster, polymerization time. However, combining the two measures, meaning that the peroxide decomposed faster and that it was dosed, resulted in a product with an average molecular weight similar to that of the conventional product and in a shortened polymerization time.

Preferably, the polymerization temperature is at most 170°C. Preferably, the reaction temperature is 150°C or lower, more preferably 130°C or lower.

The half-life of all initiators used can be determined by conventional thermal decomposition studies in monochlorobenzene, as is known in the art (see for instance the brochure "Initiators for high polymers" with code 10737 obtainable from Akzo Nobel).

By using one or more additional initiators, it was found that the same or lower residual level of monomers can be achieved compared to a conventional process that differs in that the initiators are not dosed and optimized in the dosing process.

Hence, it is preferred to not only dose the initiator but to also use one or more additional initiators. If such additional initiators are used in the process, the half-life of each of them preferably is less than 120 minutes, more preferably less than 60 minutes, even more preferably less than 30 minutes, and most preferably less than 10 minutes, and preferably more than 0.05 minutes, more preferably more than 0.5 minutes, even more preferably more than 2.5 minutes, and most preferably more than 5 minutes, in the reaction mixture at the polymerization temperature. The one or more other initiators are added to the polymerization mixture at once or they are dosed to the polymerization mixture.

10

Preferably, essentially all of the initiators that are dosed fulfill the half-life requirement. Even more preferably, essentially all initiators used in the process fulfill the half-life requirement.

15 It is noted that the word initiator is used here in the classical sense to denominate those compounds that generate free radicals, which, in turn, initiate the polymerization reaction. Hence, when certain thermally labile compounds are used for the purpose of (wholly or partially) surviving the polymerization conditions, e.g. such that they are present in the final polymer as a flame retardant
20 synergist, the part that does not decompose is not to be seen as an initiator in accordance with the present invention.

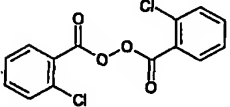
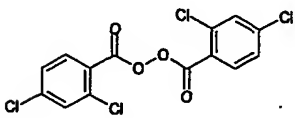
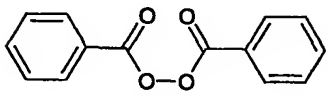
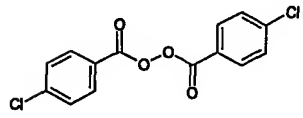
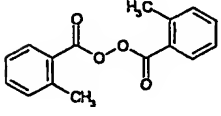
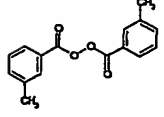
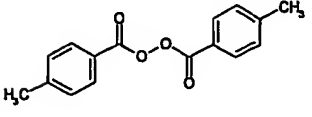
Examples of suitable classes of initiators that can be dosed and fulfill the half-life requirement for the initiator (depending on the actual polymerization temperature)
25 are peroxydicarbonates, peroxycarbonates, peroxyesters, peroxyketals, diacyl-peroxides, dialkylperoxides, azo-initiators, ketone peroxides, and mixtures thereof. These initiators may have one or more peroxy and/or azo moieties per molecule. Optionally, these initiators are further functionalized with one or more functional groups, such as amine, phosphate, ester, ether and/or alcohol groups. The
30 greatest reduction in polymerization time, while still rendering a polymer with a conventional molecular weight, was found for products selected from peroxides.

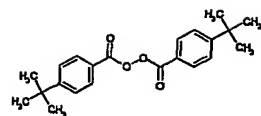
with a dibenzoylperoxide moiety or a 1,1-di(tert-butylperoxy)cyclohexane moiety and azo-initiators.

Preferred compounds with a benzoylperoxide moiety, as well as their half-lives, are presented in Table 1.

5

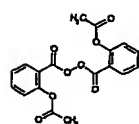
Table 1

Compound	Name	Half-life data			
		T ₁	T ₁	A	E _a
		0			
	Bis(2-chlorobenzoyl) peroxide	66	81	5.68E+19	159
	Di(2,4-dichlorobenzoyl) peroxide	55	73	4.02E+14	121.5
	Dibenzoyl peroxide	71	91	6.94E+13	122.35
	Bis(4-chlorobenzoyl) peroxide				
	Di(2-methylbenzoyl) peroxide	61	79	3.80E+14	123.4
	Bis(3-methylbenzoyl) peroxide				
	Di(4-methylbenzoyl) peroxide	70	88	5.11E+15	134.3

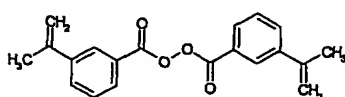


Bis(4-tert-
butylbenzoyl)
peroxide

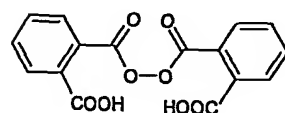
72 90 5.49E+14 128.4



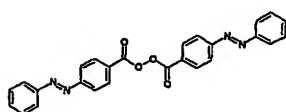
Bis(2-
acetoxybenzoyl)
peroxide



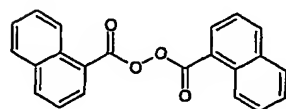
Bis(3-
isopropenylbenzoyl)
peroxide



Diphthaloyl peroxide

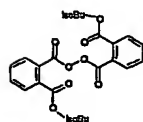


Bis(4-
phenylazobenzoyl)
peroxide



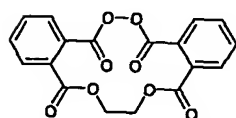
Bis(1-naphthoyl)
peroxide

47 62 1.30E+17 133.4

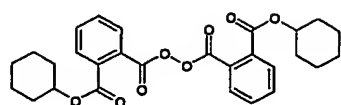


Bis(2-isobutoxy-
carbonylbenzoyl)
peroxide

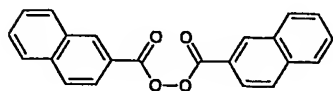
75 88 7.14E+21 176.9



1,2,7,10-Tetraoxa-
3,6,11,14-tetraoxo-
4,5,12,13-dibenzo-
cyclotetradecane



Bis((2-cyclohexyl- 74 89 1.18E+20 164.7
oxycarbonyl)benzoyl
) peroxide



Bis(2-naphthoyl) 75 92 2.90E+17 147.8
peroxide

In the table T10 is the temperature (in °C) at which the half-life of the compound is 10 hours, T1 is the temperature (in °C) at which the half-life of the compound is 1 hour, Ea is the activation energy in J/mole, and A is the Arrhenius frequency factor in s⁻¹. Using the conventional Arrhenius equation, the half-life at the polymerization
5 temperature can be calculated.

More preferred are substituted, or unsubstituted, dibenzoylperoxides, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2-di(tert-butylperoxy)butane, 1,1-di(tert-butylperoxy)cyclohexane, and azo initiators. Most preferred are
10 dibenzoylperoxide, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2'-azobis(isobutyronitrile), and 2,2'-azobis(2-methylbutyronitrile). Commercially available initiators are obtainable under trade names such as Trigonox® 99, Trigonox® SBP, Trigonox® EHP, Trigonox® 131, Trigonox® 141, Trigonox® 21S, and Perkadox® 16, Trigonox® 27, Trigonox® 22, Trigonox® 29, Trigonox® 25,
15 Trigonox® 125, Trigonox® 121, Trigonox® 421, Trigonox® 425, Perkadox® AMBN, Perkadox® AIBN, Perkadox® L W-75, Perkadox® 12, and Laurox.

The additional initiators used in the present process differ from the initiator, but may be selected from the same group of compounds.

20 When the reaction mixture is formulated at or near the polymerization temperature, which is called the warm-start process, it is not required to add a certain amount of initiator before bringing the reaction mixture to the reaction temperature and dosing the remainder at the reaction temperature. However, also in this warm-start process it may be beneficial to at once add up to 10 wt.%,
25 preferably up to 5 wt.% of an initiator, based on the combined weight of the

monomers, to the reaction mixture prior to polymerization. The initiator can then be dosed continuously or semi-continuously at the reaction temperature. When this procedure is used, the first initiator is added as the last ingredient after the monomers, solvent, and possibly other components have been mixed. This
5 procedure is particularly preferred if a certain amount of polymerization inhibitor (a radical trapping species) is present in the reaction mixture. If such radical scavenger is present, for instance because it is contained in the monomer as a constituent thereof (typically added as a stabilizer), the initially dosed initiator will react with said scavenger, thereby preventing a delayed start of the polymerization
10 reaction.

Preferably, the type and the amount of additional initiator are selected such that the residual monomer content of the final polymerized product is less than 5,000 mg/kg of monomer, preferably less than 2,000 mg/kg of monomer, more
15 preferably less than 1,000 mg/kg of monomer.

The total amount of initiator to be used in the process according to the invention is within the range conventionally used in polymerization processes. Typically, it is preferred to use at least 0.01 wt.%, more preferably at least 0.05 wt.%, and most
20 preferably at least 0.1 wt.% of all initiators and preferably at most 5 wt.%, more preferably at most 3 wt.%, and most preferably at most 1 wt.% of all initiators, based on the weight of the monomers to be polymerized.

Dosing to the reactor is typically effected by dosing the initiator as such (neat), as
25 a mixture or solution with one or more solvents, or as a dispersion. Suitable solvents are preferably selected from the group consisting of water, conventional organic solvents, monomers, blowing agents (such as pentane, isopentane, and the like), and mixtures thereof. Mixtures with monomer may not be preferred for safety or quality control reasons. Preferably dispersions of the initiator, more
30 preferably aqueous dispersions, are used. Most preferably a suspension of the initiator in water is used, such as a 40 wt.% dibenzoylperoxide suspension in water. Said suspension can be obtained commercially from Akzo Nobel Polymer

Chemicals under the trade name Perkadox® L W-40. When solvents such as alcohols are used, they can be removed during working up of the polymer after the process of polymerization. If used, advantageously solvents are used that do not adversely affect the thermal stability of the initiator dissolved therein, as can be
5 verified by analyzing the half-life temperature (temperature at which the half-life is 1 h) of the initiator in said solvent. An example of a solvent that can be used with most initiators is isododecane. If a dispersion of the initiator is dosed, the dispersion can be a dispersion of the initiator as such or a dispersion of a solution of said initiator. Preferably, the dispersion is an aqueous dispersion. Preferably,
10 dilute initiator solutions or dispersions are used that ensure rapid mixing of the initiator and the polymerization mixture, which leads to a more efficient use of the initiator. Therefore, it is preferred to use mixtures, solutions, or dispersions of the initiator having an initiator concentration of at least 0.1, more preferably at least 0.5, and most preferably at least 2 wt.%, up to at most 60, more preferably at most
15 25 wt.%, and most preferably at most 15 wt.%.

The polymerization process is a suspension process wherein the reaction mixture is a dispersion of a monomer-containing phase in a medium comprising water. In these processes the usual additives may be used. For example, for suspensions
20 in water, one or more of the usual additives such as a surfactant, a chain transfer agent, a protective colloid, an anti-fouling agent, a pH-buffer, flame retardants, flame retardant synergists, etc., may be present. Blowing agents can be added at the start of or during the polymerization process. Because of the presence of styrene monomer and blowing agents such processes are at least partially carried
25 out in a pressurized reactor. The combined weight of the additives preferably is at most 20 wt.%, based on the combined weight of all monomers.

Because of the reduced polymerization time of the present process, it is preferred to add blowing agents, if used, at an earlier stage than in a conventional process.
30 More preferably, part or all of the blowing agent is introduced to the reaction mixture when the degree of polymerization of the monomer is less than 80, preferably less than 60, and most preferably less than 50%. A suitable process

was found to be one where the blowing agent was dosed or added within one hour of the start of the polymerization. The most preferred process according to the invention is a batchwise suspension polymerization process involving the use of a blowing agent, for making expandable polystyrene (EPS).

5

In addition to the fact that dosing of the initiator at variable rates is beneficial for using the cooling capacity of the polymerization reaction in the most optimal way, it was also found that varying the dosing speed of the initiator during the polymerization process is advantageous for obtaining an economical polymerization process and obtaining polymerized product with the desired molecular weight. By varying the dosing speed within one run, polymers with a polymodal molecular weight distribution can be made. For instance, a bimodal molecular weight distribution can be produced in the same run by using two periods with varying dosing speeds. Such a bimodal molecular weight distributed polymer mixture has a part with low-molecular weight that is useful for improving the expandability of polystyrene and a part with high-molecular weight that improves the mechanical properties of the polymer.

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Furthermore, it was observed that a polymer with essentially the same molecular weight as from a conventional process can be produced in less time, the only differences being the controlled dosing of the initiator and optimizing of the initiators used in the dosing process.

20

After the polymerization, the resulting (co)polymer (or resin) is preferably treated as is usual in the art. Polymers so obtained can be submitted to the usual monomer reduction, drying and/or screening steps. These one or more steps can be followed by, for example, an expansion step. As in conventional EPS processes, the amount of residual monomer content in the polymer product can be reduced in the usual manner; preferably by including a second step in the process wherein the reaction temperature is higher than the temperature used in the first step wherein the initiator was dosed, typically approx. 110-170°C, preferably in the presence of one or more additional initiators with half-life

25

30

temperatures as defined before, such as tert-butylperoxybenzoate, tert-butyl peroxy-2-ethylhexyl carbonate, dicumylperoxide, or tert-amyl peroxy-2-ethylhexyl carbonate. These additional initiators may be added at the start of or during the polymerization process. The resulting resin is characterized in that it preferably
5 contains less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening.

The resulting resin is further characterized in that it preferably has a weight
10 average molecular weight (Mw) of at least 100,000 g/mol, more preferably of at least 125,000 g/mol, and most preferably of at least 150,000 g/mol, and that it has a Mw preferably of at most 500,000 g/mol, more preferably of at most 450,000 g/mol, and most preferably of at most 350,000 g/mol, measured in accordance with conventional gel permeation chromatography techniques using polystyrene
15 standards.

The invention further relates to styrene based (co)polymer obtainable by the aforementioned process and to the use of the styrene (co)polymer in a shaping process involving the heating of the co(polymer) for the preparation of foamed articles.
20

The invention is illustrated by the following non-limitative examples.

Examples 1-4 and Comparative Examples A-D

25 General for Experiments 1-4 and A-D:

BPO, Px L	(Perkadox® L W-75) Dibenzoyl peroxide (the initiator) ex Akzo Nobel
Tx-117	(Trigonox® 117) Tert-butylperoxy 2-ethylhexylcarbonate (additional initiator) ex Akzo Nobel
30 Tx-131	(Trigonox® 131) Tert-amylperoxy 2-ethylhexylcarbonate (additional initiator) ex Akzo Nobel

A temperature-controlled 1-liter stainless steel Büchi reactor equipped with a baffle, a three-blade stirrer, a pressure transducer, (an) initiator dosing line(s), and a nitrogen purge was charged with 1.25 g of tricalcium phosphate. Then a solution of 230 g of water, 20 g of a 0.1 wt.% Nacconol® 90G (ex Stephan Chemie Co.) solution in water, and 10 g of a 0.5 wt.% Gohsenol® C500 (ex Nippon Gohsei) solution in water was added and stirred for approximately 5 min. To the reactor 220 g of styrene monomer were added. The reactor was evacuated several times to remove oxygen, a nitrogen blanket was applied, the reactor was closed, pressurized, and heated to the polymerization temperature in 45 minutes. For Comparative Examples A-D the polymerization temperature was 90°C. After 255 minutes at 90°C the temperature was raised to 120°C over a period of 60 minutes. This temperature was maintained for 120 minutes. Then, the whole was cooled to room temperature.

In Examples 1-4 the initiator was dosed, using a pressure pump, at a polymerization temperature of 110°C. In examples where no pentane was used, Perkadox® L W-75 was dosed in 90 minutes as a solution in 30 g styrene. The additional initiator was added as a solution in 5 g styrene after 190 minutes over a period of 15 minutes. In the examples where pentane was used, the BPO was added as a solution in styrene and pentane (30g/15g) and the additional initiator was added as a solution in 5 g pentane after 190 minutes of polymerization time over a period of 15 minutes. In all examples 1-4 the temperature was increased, after 190 min polymerization time at 110°C, in 30 minutes to 120°C. This temperature was maintained for 80 minutes. Then, the content of the reactor was cooled to room temperature.

25

The results are collected in the table below. It can be concluded that by dosing of the initiator (Examples 1-4), EPS with the same average molecular weight (M_w and M_n) and polydispersity can be obtained as in examples wherein the initiator is not dosed and the temperature is lower (Comp. Examples A-D). In dosing experiments where no pentane is used (Examples 3-4) also the same low residual

30

styrene values are obtained as in non-dosing examples where no pentane is used (Comp. Examples C-D).

Examples 5-9 and Comparative Example E:

Px-BC (Perkadox® BC-FF) Dicumyl peroxide ex Akzo Nobel

5 The procedure of the previous examples was repeated, except that 260 g of water was charged. In Examples 5, 8, and 9, additional initiator was added to the polymerization reaction at 180, 160, and 135 minutes after the start of the reaction, respectively. In Examples 6, 7, and E, the additional initiator was added at once prior to the start of the polymerization.

10 In examples 5 and 8 the temperature was increased after 190 min polymerization time at 110°C, in 15 minutes (example 5) or 30 minutes (example 8) to 120°C. This temperature was maintained for 50 minutes (example 5) or 80 minutes (example 8).

15 In example 7 the temperature was increased after 175 min polymerization time at 110°C, in 60 minutes to 130°C. This temperature was maintained for 100 minutes. In example 6 the temperature was increased after 155 min polymerization time at 110°C, in 30 minutes to 120°C. This temperature was maintained for 65 minutes, followed by an increase in temperature to 150°C in 15 minutes at which this temperature was maintained for 95 minutes.

20 The results are collected in the table below. It can be concluded that the polystyrene obtained in a polymerization process according to the invention is comparable with respect to molecular weight and molecular weight distribution to polystyrene obtained in a conventional process, but the process of the invention requires a shorter polymerization time.

(Comparative) Example	5	6	7	8	9	E
Initiator	Px-L W75	Px-L W75	Px-L W75	Px-L W40	Px-L W40	Px-L W75
Additional initiator	Tx-131	Tx-117	Px-BC	Tx-131	Tx-131	Tx-117
Mw product (x 1000) g/mol	260	229	231	284	279	243
Mn product (x 1000) g/mol	84	75	72	92	102	101
D (Mw/Mn)	3.1	3.1	3.2	3.1	2.8	2.7
Residual styrene (wt. %)	0.28	0.10	0.50	0.17	0.07	0.31
Polymerization time	300	370	325	300	300	480
Amount BPO (meq/100g styrene)	1.24	0.83	1.53	1.24	0.98	0.98
Dosing time BPO (min)	90	90	90	75	80	0
Amount add. initiator (meq/100g styrene)	0.46	0.87	0.46	0.46	0.46	0.46
Dosing time add. initiator (min)	15	0	0	5	5	0
Initial temperature (°C)	110	110	110	110	110	90
Max. polymerization temperature (°C)	120	150	130	120	120	120

Examples 10-11

Px L W40 (Perkadox®-L W40-TCP) Dibenzoyl peroxide suspension ex Akzo Nobel

- 5 The procedure of Example 5 was repeated, except that no additional initiator was used. In example 10 Px L W40 was used. The peroxide suspension was dosed as a diluted suspension (in 30 g water, the intake of water at the start of the reaction was corrected for this amount). Perkadox® L W-75 was used in example 11 and dosed as a solution in 30 g styrene. The styrene solution had to be temperature
- 10 controlled in order to avoid polymerization of the solution itself.

The results were as follows:

	Example 10	Example 11
Conversion (%)	99.0	83
Residual monomer (%)	1.02	17
Mw	245000	185000
Mn	88000	70000
Dispersity	2.8	2.6

- It can be concluded that the use of a suspension of BPO is preferred over the use
- 15 of a solution of BPO in the process of the invention.

CLAIMS

1. An essentially vinyl chloride-free suspension polymerization process for polymerizing styrene monomer, or a mixture of monomers comprising styrene, comprising the step of continuously or semi-continuously dosing an initiator, or a mixture of initiators, to the reaction mixture at the polymerization temperature, characterized in that at least one initiator that is dosed has a half-life of 60 minutes or less at said polymerization temperature.
2. Process according to claim 1 wherein the composition further comprises co-monomers selected from the group consisting of vinyl acetate, ethylene, propylene, acrylonitrile, butadiene, (meth)acrylates, and ethylenically unsaturated polymers, such as polybutadiene and styrene butadiene rubber.
3. Process according to claim 1 or 2 wherein said initiator is dosed continuously or semi-continuously from the point in time at which at least 1%, preferably at least 0.5%, more preferably at least 0.1%, most preferably none of the monomer has already been polymerized until at least 70%, preferably at least 80%, more preferably at least 90%, and most preferably essentially all of the monomer is polymerized, the term "essentially all of the monomer is polymerized" meaning that less than 1,000 ppm of monomer is present in the final polymerized product.
4. Process according to any one of claims 1-3 wherein the initiator is selected from the group consisting of peroxydicarbonates, peroxycarbonates, peroxyesters, peroxyketals, diacylperoxides, dialkylperoxides, ketone peroxides, azo-initiators, each of which can have one, two, or more -OO-, and/or -NN- moieties in each molecule, and each of which is optionally further functionalized with amines, phosphates, esters, ethers, or alcohol moieties, and mixtures thereof, said initiators being preferably selected

from the group consisting of substituted, or unsubstituted, dibenzoylperoxides, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2-di(tert-butylperoxy)butane, 1,1-di(tert-butylperoxy)cyclohexane, azo initiators, and mixtures thereof, most preferably from dibenzoylperoxide, 1,1-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-methylbutyronitrile), and mixtures thereof.

5. Process according to any one of claims 1-4 wherein the reaction temperature is 170°C or lower, preferably 150°C or lower, more preferably 130°C or lower, and most preferably 120°C or lower.
6. Process according to any one of claims 1-5 wherein at least part of the initiator is continuously or semi-continuously dosed over a period of at least 0.5 hour, preferably at least 1 hour.
7. Process according to any one of claims 1-6 wherein at least 0.01 wt.%, more preferably at least 0.05 wt.%, and most preferably at least 0.1 wt.% of the combined weight of all initiators and preferably at most 5 wt.%, more preferably at most 3 wt.%, and most preferably at most 1 wt.% of the combined weight of all initiators, based on the weight of the monomers to be polymerized, is used.
8. Process according to any one of claims 1-7 wherein a blowing agent is added or dosed to the reaction mixture when the degree of polymerization of the monomer is less than 80%, preferably less than 60%, and most preferably less than 50%.
9. Process according to any one of claims 1-8 wherein the initiator, or mixture of initiators, is dosed in the form of a, preferably aqueous, dispersion.

10. Process according to any one of claims 1-9 wherein an additional initiator is used to reduce the residual monomer level.
- 5 11. Process according to claim 10 for the preparation of expandable polystyrene.
- 10 12. Styrene based (co)polymer obtainable by a process according to any one of claims 1-11, wherein the styrene based (co)polymer has less than 50 ppm of residual initiator, more preferably less than 40 ppm, and most preferably less than 25 ppm of initiator, immediately after drying for 1 hour at 60°C and screening.
- 15 13. Use of a styrene (co)polymer according to claim 12 in a shaping process involving the heating of the co(polymer) for the preparation of foamed articles.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DOSING OF PEROXIDE TO A SUSPENSION PROCESS WHEREIN STYRENE IS POLYMERIZED

(57) Abstract: The invention relates to a suspension polymerization process for the preparation of styrene-containing (co)polymers, wherein the process comprises the steps of continuously or semi-continuously dosing an initiator to the reaction mixture, said initiator having a specified half-life at the temperature of the reaction mixture to which it is dosed. The invention further relates to styrene based (co)polymer obtainable by said process, and to the use of said styrene (co)polymer in a shaping process.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F12/08 C08F257/02 C08F2/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F F21V C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 189 069 A (BRETSCHNEIDER JUERGEN ET AL) 23 February 1993 (1993-02-23) * abstract ; claim 1 ; column 2, line 20-32 ; column 3, line 33-37, 48-66 *	1-11
X	US 3 451 985 A (MAHLO EDWIN K) 24 June 1969 (1969-06-24) * column 2, line 9-22 ; column 4, line 54-59 "styrene" ; column 1, line 11-46 ; claims 1-3 *	1-10
X	US 4 363 881 A (SMITH STUART B) 14 December 1982 (1982-12-14) * claims 9-15 ; column 3, line 16-21, 29-32, 41-59 ; column 4, line 25-28 *	1-5,7-11
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/003661

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 086 591 A (MONSANTO CO) 11 October 1967 (1967-10-11) * claims 1-4 ; example 5 ; page 2, line 83-90 ; page 2, line 17-64 *	1-7,9
X	----- WO 02/14393 A (BASF AG ; KUEHN INGOLF (DE); SCHUHMACHER RUDOLF (DE)) 21 February 2002 (2002-02-21) * claims 5, 1-4 ; page 5, line 13-18 ; page 4, line 23-29 ; abstract ; page 3, line 3 - page 4, line 2 *	1-7,9,10
X	----- US 5 905 096 A (BAUMGAERTEL MICHAEL ET AL) 18 May 1999 (1999-05-18) * Example 1 ; claims 1-10 ; column 2, line 13 - column 3, line 6 *	1-11
X	----- WO 00/17245 A (AKZO NOBEL NV ; SCHUT JACOBUS (NL); WESTMIJZE HANS (NL); SWIETEN ANDRE) 30 March 2000 (2000-03-30) * abstract ; page 2, line 11-16 ; page 3, line 12 - page 6, line 13 ; page 2, line 24 "styrene".	1-10
X	----- EP 0 390 000 A (IDEMITSU PETROCHEMICAL CO) 3 October 1990 (1990-10-03) * column 2, line 30 - column 3, line 33 ; column 7, line 15, 21-26 ; abstract ; column 5, line 47 - column 6, line 54 ; claims 1,4,5 *	1-7,9,10
A	----- US 4 731 388 A (OHGI SHINYA ET AL) 15 March 1988 (1988-03-15) * claims 1,8-10 ; column 3, line 45 - column 4, line 64 ; examples *	1-11
A	----- EP 0 488 025 A (KANEFUCHI CHEMICAL IND) 3 June 1992 (1992-06-03) * page 3, line 56 - page 4, line 6 ; examples *	1-11
A	----- DE 199 11 960 A (BASF AG) 21 September 2000 (2000-09-21) * claims 1-8 *	1-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2004/003661

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of Item 3 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 11

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-11

An "essentially vinyl chloride-free" suspension polymerisation process for polymerising styrene monomer, or a mixture of monomers comprising styrene, comprising the step of continuously or semi-continuously dosing an initiator, or a mixture of initiators, to the reaction mixture at the polymerisation temperature, characterised in that at least one initiator that is dosed has a half-life of 60 minutes or less at said polymerisation temperature.

2. claim: 12

Styrene based (co) polymer "obtainable" by a process as described in the application claim 12.

3. claim: 13

The use in a shaping process for the preparation of foamed articles of a styrene (co) polymer as described in application claim 13.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2004/003661

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5189069	A	23-02-1993	DE 4029298 A1 BR 9103948 A CA 2051324 A1 CN 1059912 A DE 59105698 D1 EP 0476256 A1 ES 2073075 T3 FI 914278 A JP 4279607 A KR 161984 B1 MX 174341 B NO 913632 A	19-03-1992 26-05-1992 16-03-1992 01-04-1992 20-07-1995 25-03-1992 01-08-1995 16-03-1992 05-10-1992 15-01-1999 09-05-1994 16-03-1992
US 3451985	A	24-06-1969	DE 1570963 A1 FR 1439957 A GB 1086591 A JP 52039074 B	02-03-1972 27-05-1966 11-10-1967 03-10-1977
US 4363881	A	14-12-1982	AU 7785481 A DK 523381 A EP 0053039 A1 ES 8303487 A1 FI 813754 A JP 57172936 A NO 813984 A ZA 8108026 A	03-06-1982 27-05-1982 02-06-1982 01-05-1983 27-05-1982 25-10-1982 27-05-1982 27-10-1982
GB 1086591	A	11-10-1967	DE 1570963 A1 FR 1439957 A JP 52039074 B US 3451985 A	02-03-1972 27-05-1966 03-10-1977 24-06-1969
WO 0214393	A	21-02-2002	DE 10039388 A1 BR 0113153 A CN 1446233 T WO 0214393 A1 EP 1309636 A1 US 2003187135 A1	21-02-2002 08-07-2003 01-10-2003 21-02-2002 14-05-2003 02-10-2003
US 5905096	A	18-05-1999	DE 19530765 A1 AU 6822496 A CA 2227270 A1 CN 1193986 A CZ 9800501 A3 DE 59602118 D1 WO 9708231 A1 EP 0846141 A1 ES 2133196 T3 JP 11513056 T NO 980736 A PL 325059 A1	27-02-1997 19-03-1997 06-03-1997 23-09-1998 15-07-1998 08-07-1999 06-03-1997 10-06-1998 01-09-1999 09-11-1999 20-02-1998 06-07-1998
WO 0017245	A	30-03-2000	AU 756065 B2 AU 5862499 A BR 9913993 A CA 2344824 A1 CN 1323323 T WO 0017245 A1	02-01-2003 10-04-2000 03-07-2001 30-03-2000 21-11-2001 30-03-2000

INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0017245	A		EP 1124866 A1	22-08-2001
			HU 0104277 A2	28-03-2002
			ID 29411 A	30-08-2001
			JP 2002526574 T	20-08-2002
			NO 20011413 A	03-05-2001
			PL 346757 A1	25-02-2002
			SK 3982001 A3	03-12-2001
			TR 200101491 T2	21-12-2001
			US 2002123591 A1	05-09-2002
			US 6384155 B1	07-05-2002
			ZA 200102333 A	20-06-2002
EP 0390000	A	03-10-1990	JP 2255708 A	16-10-1990
			AT 100474 T	15-02-1994
			AU 622784 B2	16-04-1992
			AU 5226890 A	04-10-1990
			CA 2013283 A1	30-09-1990
			DE 69006063 D1	03-03-1994
			DE 69006063 T2	19-05-1994
			EP 0390000 A2	03-10-1990
			ES 2050294 T3	16-05-1994
			FI 99018 B	13-06-1997
			KR 9512722 B1	20-10-1995
			US 5032650 A	16-07-1991
US 4731388	A	15-03-1988	JP 1853592 C	07-07-1994
			JP 5073132 B	13-10-1993
			JP 62169836 A	27-07-1987
			JP 1852462 C	21-06-1994
			JP 5073133 B	13-10-1993
			JP 62185721 A	14-08-1987
			EP 0234705 A2	02-09-1987
EP 0488025	A	03-06-1992	JP 2933707 B2	16-08-1999
			JP 4185616 A	02-07-1992
			CA 2055082 A1	22-05-1992
			DE 69122841 D1	28-11-1996
			DE 69122841 T2	03-04-1997
			EP 0488025 A2	03-06-1992
			US 5132330 A	21-07-1992
DE 19911960	A	21-09-2000	DE 19911960 A1	21-09-2000